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(54) Flameproofing of Hardwood by A Low-pressure Process

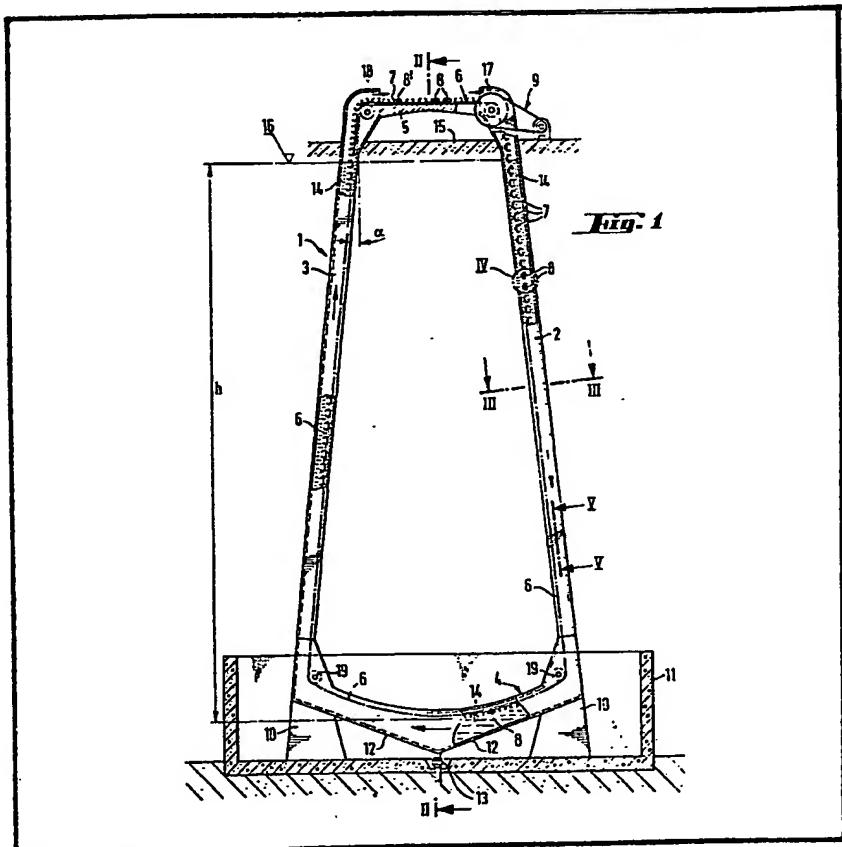
(57) A process for flameproofing hardwood is described in which the wood is treated with an aqueous formulation, preferably by dipping, under a static excess pressure of 0.3 to 2.5 bars, the formulation containing
(a) at least one flameproofing agent, for example ammonium salts of phosphoric acid,
(b) optionally a fixing agent, for example thickeners of natural or synthetic origin or reaction products of

at least urea or cyanamides and formaldehyde and

(c) optionally a blowing agent, for example urea or derivatives thereof.

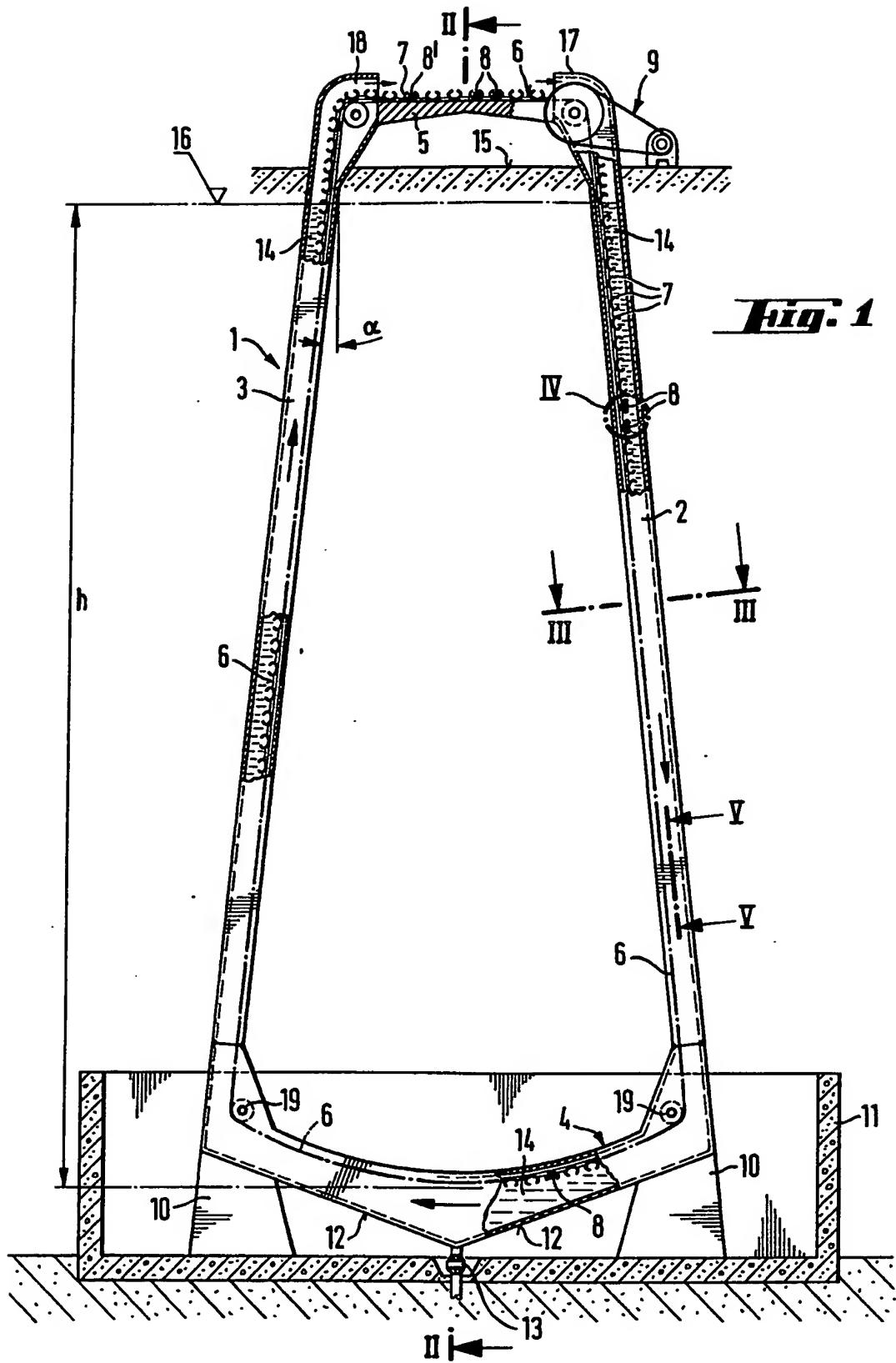
An apparatus for carrying out the process by dipping in a continuous procedure comprises a U shaped tube 1 filled with treating liquid to a depth h of 3 to 25 metres and containing a conveyor in the form of chains 6 and carrier rails 7 to move timbers 8 through the tube.

The treated wood has a permanent flameproof finish and is used in particular in the form of eucalyptus timber in mining.



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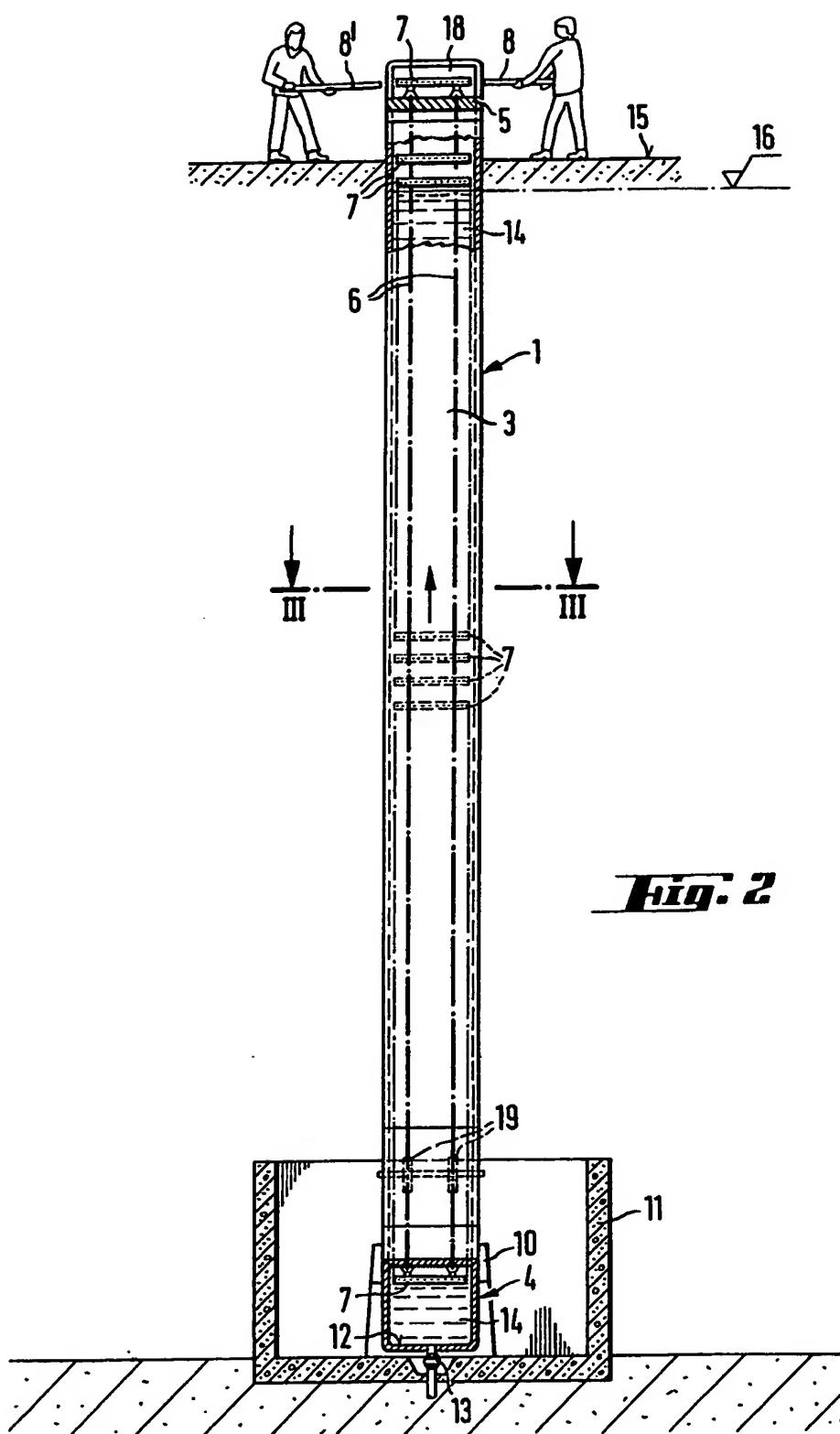
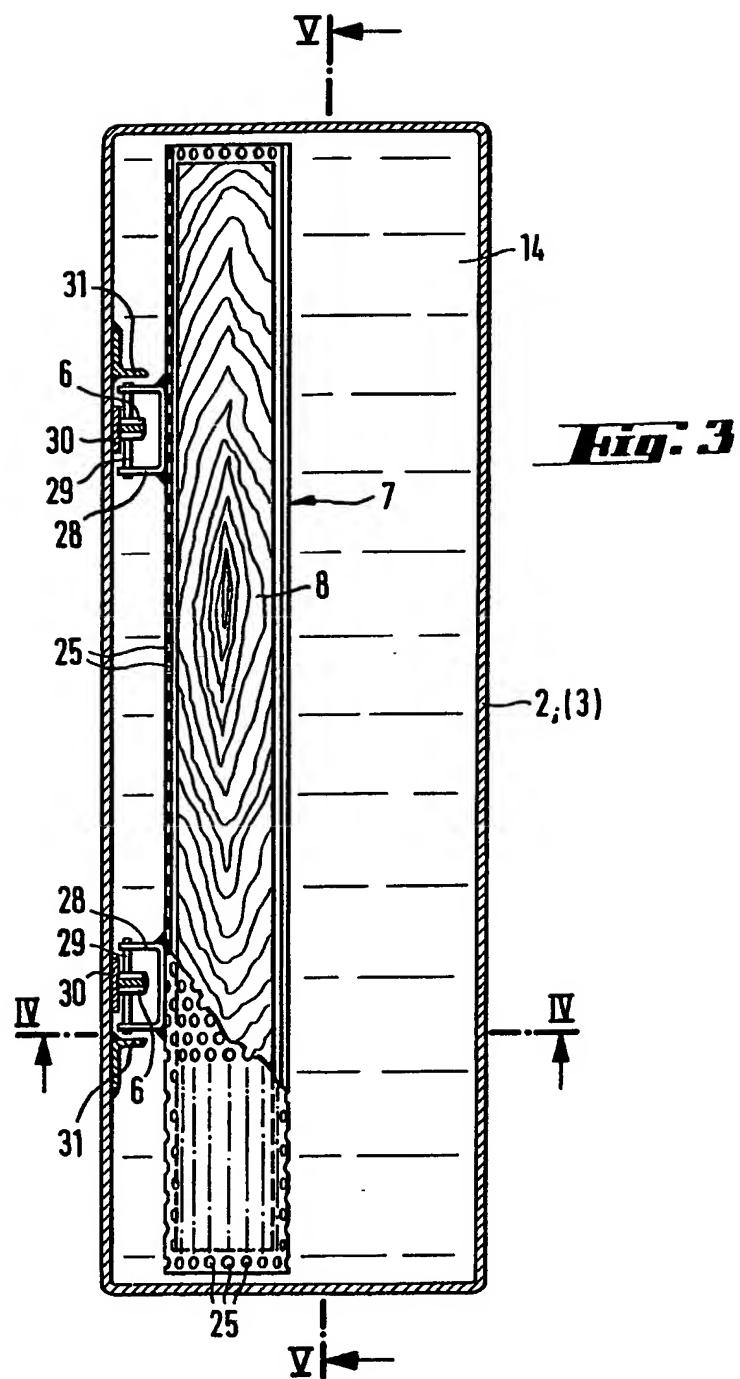


Fig. 2

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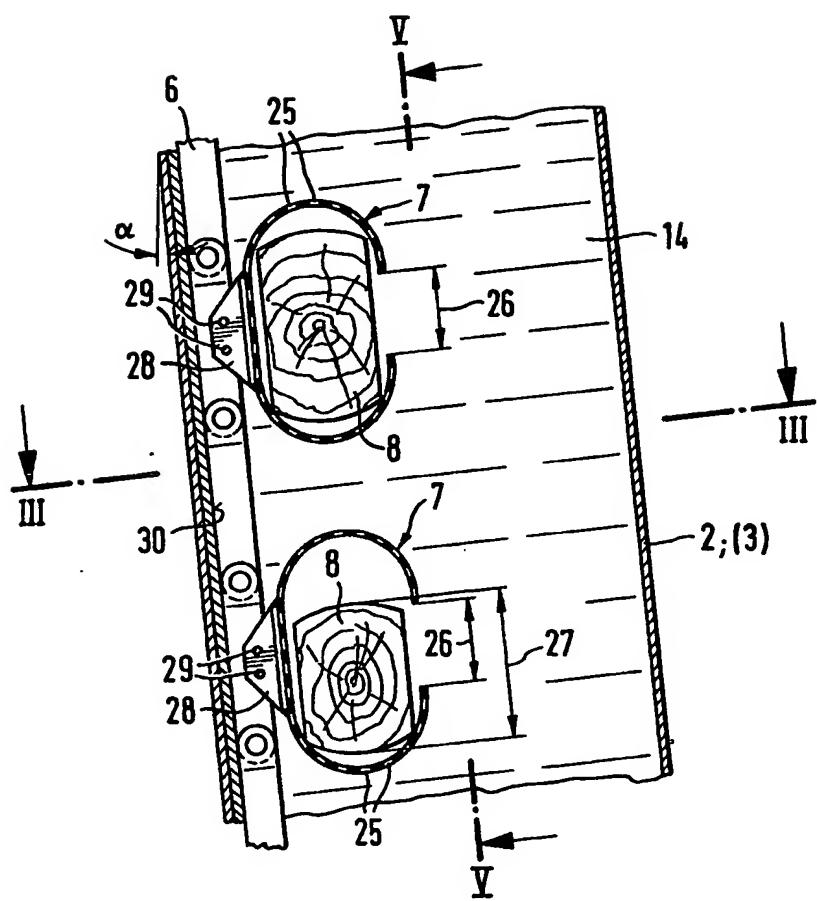
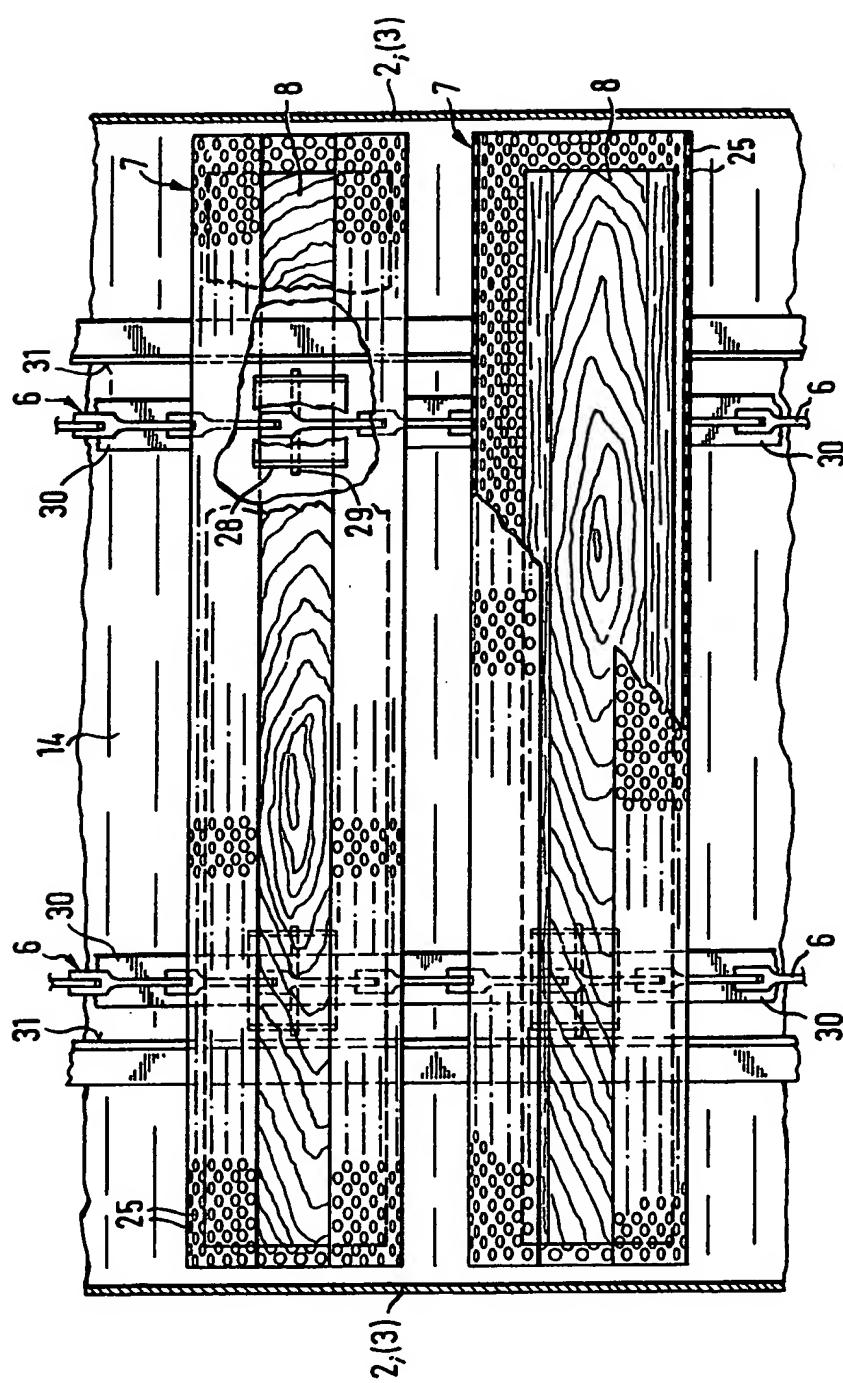


Fig. 4

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SPECIFICATION
Flameproofing of Hardwood by a Low-pressure Process

The present invention relates to the flameproofing of hardwood.

In general, flameproofing of hardwood, for example eucalyptus wood, is carried out using a high excess pressure. Thus, for example, B. A. Richardson, on page 105 of the handbook "Wood preservation", The Construction Press (1978), describes the use of an excess pressure of 50 to 70 bars when flameproofing impermeable types of eucalyptus wood.

In contrast to the above, in the process according to the invention hardwood is unexpectedly provided with a flameproof finish using a low excess pressure of not more than 2.5 bars, with a saving in the corresponding energy costs.

The present invention thus relates to a process for flameproofing hardwood using formulations containing aqueous flameproofing agents, which comprises treating hardwood under an excess pressure of 0.3 to 2.5 bars with aqueous formulations which contain

- (a) at least one flameproofing agent,
- (b) optionally at least one fixing agent and
- (c) optionally at least one blowing agent.

The formulation for carrying out the process, insofar as this contains not less than two of the components (a), (b) and (c), the hardwood provided with a flameproof finish using the process, and the use of this hardwood as timber in mining, constitute further subjects of the present invention.

The excess pressure required in the process can be obtained either in a closed apparatus, for example in a pressure vessel of conventional construction, or preferably by dipping the wood beneath the surface of the formulation. In the latter case, a static excess pressure is set up, and this is proportional to the depth below the level of the liquid. In this preferred embodiment of the process, thus, the wood is dipped 3 to 25, and in particular 8 to 16, m deep into the formulation containing the flameproofing agent in order to effect treatment of the wood under a static excess pressure of 0.3 to 2.5 and in particular 0.8 to 1.6 bars.

Insofar as the process is carried out in its preferred embodiment, by dipping the wood into the formulation, an apparatus for carrying out the process, which feeds the wood from the surface down to the desired depth beneath the liquid and, after impregnation of the wood is complete, feeds the wood back up to the surface of the formulation again in a continuous procedure, constitutes a further subject of the present invention.

In principle, all commercially available flameproofing agents for the treatment of wood are suitable as compulsorily used component (a) of the formulation for carrying out the process according to the invention. In general, such flameproofing agents contain inorganic salts, such as monoboric or tetraboric acid and the sodium salts thereof, ammonium salts of ortho- and meta-phosphoric acid, ammonium bromide, ammonium sulfate, ammonium bisulfate and ammonium sulfamate, calcium chloride, calcium sulfate, magnesium chloride, magnesium sulfate, tin chloride, tin sulfate, zinc chloride and zinc sulfate, sodium chromate and sodium dichromate and aluminium hydroxide. Preferred salts are water-soluble inorganic salts, such as calcium chloride, magnesium chloride, borax, ammonium sulfate, ammonium sulfamate, ammonium polyphosphate, ammonium dihydrogen phosphate and ammonium hydrogen phosphate; ammonium hydrogen phosphate and ammonium dihydrogen phosphate, which have the advantage of forming aqueous solutions with a pH of 4 to 7 which do not damage the wood to be treated, are of primary interest.

The optional component (b) of the formulations employed for carrying out the process according to the invention can be thickeners or reaction products of urea or cyanamides and formaldehyde, and the thickeners can be of either natural or synthetic origin.

Examples of thickeners of natural origin are digested, etherified, esterified or cationically or anionically modified starches, preferably maize starch, potato starch, wheat starch and rice starch or their degradation products, for example dextrans, especially digested maize, potato, wheat and rice starch, i.e. maize, potato, wheat and rice starch which has been at least partially degraded under the action of hot water and if desired in the presence of an inorganic acid, such as sulfuric acid and hydrochloric acid, or the hydroxyethyl derivatives of the said starches, pectins and flours of vegetable origin, especially of guar flour or carob bean flour, sizes of animal origin, especially bone gelatin, alginic acid and the salts and esters thereof, especially a sodium alginate, and cellulose esters or cellulose ethers and salts thereof, especially a methyl- or carboxyethyl-cellulose and the sodium salts thereof. Digested starches and their derivatives are particularly preferred.

Examples of thickeners of synthetic origin are polyacrylic acids and polyvinyl or polyacrylic derivatives, especially polyacrylic acids and sodium polyacrylates or ammonium polyacrylates and polyvinyl alcohols. Polyacrylic acids with molecular weights of 800,000 to 2,000,000 are particularly preferred.

If reaction products of the indicated type are employed as the optional component (b), these reaction products are prepared from

- (b₁) urea, cyanamide or dicyandiamide,
- (b₂) formaldehyde or a formaldehyde donor,
- (b₃) optionally an ammonium salt and
- (b₄) an alkylene polyamine of at most 18 carbon atoms, or an acid salt thereof,

and these reaction products can be in the form of solutions in water and/or an alkanol having 1 to 4 carbon atoms in particular isopropanol or

ethanol, and especially methanol. Both aqueous and alcoholic or preferably aqueous-alcoholic solutions can be used.

Cyanamide is preferred to urea and

5 dicyandiamide as component (b₁) for the preparation of the reaction products (b).

The formaldehyde donors, as component (b₂) for the preparation of the reaction products (b), are, for example, hexamethylolmelamine, trioxan

10 and in particular paraformaldehyde.

Formaldehyde in the form of the actual compound is preferred to the formaldehyde donors as component (b₂).

The ammonium salts used as the optional

15 component (b₃) for the preparation of the reaction products (b) are the same as the salts employed as component (a), insofar as the preferred salts (b₃) employed are monomeric ammonium salts of metaphosphoric acid and in particular of ortho-phosphoric acid, such as ammonium dihydrogen phosphate and ammonium hydrogen phosphate. However, the ammonium salts which are of primary interest as the optional component (b₃) are derived from organic acids, such as formic

20 acid or acetic acid, or mineral acids, such as nitric acid and in particular hydrochloric acid, and thus differ from the components (a) employed as the flameproofing agents. Accordingly, the ammonium salts used as component (b₃) are, in

25 particular, ammonium formate, ammonium acetate, ammonium nitrate and especially ammonium hydrogen phosphate, ammonium dihydrogen phosphate and ammonium chloride, ammonium chloride being of primary interest.

30 Preferred polyamines for the optional component (b₄) for the preparation of the reaction products (b) are alkylene-diamines, -triamines or -tetramines having 2 to 6 carbon atoms in the alkylene radical. Suitable alkylene-diamines,

35 -triamines or -tetramines are thus trihexamethylenetetramine, tripentylmethylenetetramine, tributylene-tetramine, tripropylenetetramine and triethylenetetramine, in particular dihexamethylene-triamine, dipentylene-triamine, dibutylenetriamine, dipropylene-triamine and diethylene-triamine and especially hexamethylenediamine, pentylene-diamine, butylene-diamine, propylene-diamine and ethylene-diamine. Ethylenediamine is of primary

40 interest. Suitable acid salts of these polyamines are, in particular, halides and especially the hydrochloride.

Preferred optional components (b) are thus, for example, reaction products of

45 (b₁) urea, cyanamide or dicyandiamide,

(b₂) formaldehyde or paraformaldehyde,

(b₃) optionally ammonium chloride, ammonium acetate, ammonium formate, ammonium nitrate, ammonium hydrogen phosphate or ammonium

50 dihydrogen phosphate and

(b₄) optionally ethylenediamine or a halide thereof, and these reaction products can be in the form of aqueous-methanolic, aqueous-ethanolic or aqueous-isopropanolic solutions.

55 Reaction products of primary interest are

reaction products of

(b₁) 2 mols of dicyandiamide,

(b₂) 1 mol of paraformaldehyde and

(b₃) 1 mol of ammonium dihydrogen phosphate

70 or 1 mol of ammonium nitrate, reaction products of

(b₁) 1 mol of dicyandiamide,

(b₂) 1.0 to 2.2 mols of formaldehyde,

(b₃) 0 to 0.8 mol of ammonium chloride and

(b₄) 0.1 to 0.5 mol of ethylenediamine or ethylenediamine dihydrochloride, and in particular reaction products of

(b₁) 1 mol of dicyandiamide,

(b₂) 2.0 to 2.3 mols of formaldehyde and

(b₃) 1.0 to 1.3 mols of ammonium chloride, which are preferably in the form of aqueous or aqueous-methanolic solutions.

The reaction products used as the optional component (b) and the preparation of these reaction products, are known per se and are described, for example, in German Offenlegungsschrift 2,729,276 and in British Patent Specifications 1,146,484 and 1,409,460.

The additional use of a fixing agent as the optional component (b), in addition to the flameproofing agent used as component (a), is advantageous in order, if necessary, to bind the flameproofing agent more powerfully to the wood substrate and thus to increase the stability of the flameproofing effect to rinsing and spraying or weathering.

Substances suitable as optional component (c) in the formulation employed for carrying out the process according to the invention are so-called blowing agents, preferably water-soluble nitrogen compounds which, when subjected to heat, split off at least ammonia and carbon dioxide. Such compounds are, inter alia, in particular urea, urea derivatives and salts thereof. Examples of urea derivatives are, in particular, dicyandiamide, guanidine, guanylurea and melamine. Suitable salts are, for example, phosphates and in particular hydrochlorides. Urea and its derivatives of the indicated type decompose at temperatures of about 120 to about 270°C, with the elimination of ammonia, carbon dioxide and water. Guanidine and, in particular, urea are particularly preferred because of their low decomposition temperatures (about 160°C for guanidine and about 130°C for urea).

As a rule, blowing agents, as optional component (c), are employed only when a fixing agent, as optional component (b), in the form of a thickener is also used. In this preferred embodiment of the process according to the invention, in which the formulation employed contains, in addition to the flameproofing agent as component (a), a thickener as component (b), which at the same time is a fixing agent, and also blowing agent as component (c), there is obtained inside the wood a swelling coagulated material (similar to the "intumescent coatings" on surfaces), and on exposure to flame, this coagulated material, in the form of a viscous, foaming, tacky and incombustible mass, which

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may be carbonised, particularly effectively counters, spreading of the flames.

The formulation for carrying out the process according to the invention as a rule contains 20 to 5 300 g/l, and preferably 30 to 300, g/l of component (a), 0 to 60, and preferably 0.5 to 30, g/l of component (b) and 0 to 150, and preferably 10 to 100, g/l of component (c).

If the optional component (b) is used in 10 addition to component (a), the weight ratio of component (a) to component (b) is preferably 1:0.02 to 1:0.3.

If the optional component (c) is used in 15 addition to components (a) and (b), a fixing agent in the form of a thickener being employed as component (b), the weight ratio of component (b) to component (c) is preferably 1:0.03 to 1:0.6.

Since the preferred flameproofing agents (a) 20 are soluble in water, the formulation is preferably in the form of an aqueous solution, the pH value of which is as a rule not below 4 and in particular 4 to 6.

In the process according to the invention, the wood can be treated with the aqueous 25 formulations either at elevated temperatures or at room temperature, i.e. at from about 10°C to about 90°C. The higher temperatures are advisable in particular for formulations which contain fixing agents, and in this case the type 30 and concentration of the fixing agents are so chosen that the formulation is in the form of an aqueous solution only at these higher temperatures and, as a solution, penetrates into the pores of the wood and, after impregnation and 35 during drying, precipitates in the pores of the wood at room temperature. However, it is preferred to treat the wood at room temperature with formulations in the form of aqueous solutions, electing for this purpose water-soluble 40 flameproofing agents which are sufficiently effective, so that energy costs can be lowered and no heating units are required for the apparatus for carrying out the process.

The treatment time and the liquor ratio used 45 when impregnating the wood vary within wide limits and depend on the type, the stage of processing, the hardness and the water absorption of the wood employed. Treatment of the wood with the formulation under the indicated excess pressure is carried out, for 50 example, for 1 to 30, and preferably 2 to 12, minutes.

The wood which is provided with a flameproof 55 finish by the process according to the invention may be in very diverse stages of processing, for example in the form of shingles, boards or beams or timber (building timber). Suitable hardwood is wood from deciduous trees, for example beech wood, oak wood or obeche wood and in particular eucalyptus wood.

In addition, inter alia, to use in the furniture industry, the use of the wood provided with a flameproof finish according to the invention as building timber and in particular as mining timber 60 is of primary interest. The mining timber is in

particular hard gum and saligna timber.

The moisture content of the wood to be provided with a finish varies within wide limits. In the case of the preferred eucalyptus timbers, it is, for example, about 10 to 50 per cent by weight. The higher the moisture content, the lower is the liquor pick-up on impregnation.

The most important advantage of the present invention is that flameproof finishes which are 70 resistant to rinsing, i.e. permanent flameproof finishes, are already obtained even with low liquor pick-ups of about 5 to 25, and preferably 10—20, per cent by weight. The flameproof properties of the finished wood are assessed on the basis of the 75 flameproofing agent content of the wood, and this varies within wide limits depending on the type of flameproofing agent used. On the assumption that, as preferred flameproofing agents, ammonium salts of phosphoric acid are 80 employed, CSIR (Council for Scientific and Industrial Research of the National Building Research Institute in Johannesburg) Report No 50090596 (86) of May 1979 states that a phosphorus content in the finished wood of about 85 0.6 to 0.8 per cent by weight is regarded as being sufficient to achieve a good flameproofing effect in large scale fire test under conditions approximating to those encountered in practice.

In the process according to the invention, this 90 requisite flameproofing agent content is obtained using a low excess pressure and with corresponding low liquor pick-ups, this low liquor pick-up being particularly advantageous because it renders drying of the wood superfluous in 95 mining. Moreover, because of the pH value of the impregnating liquors, which as a rule is not below 4 and preferably is 4 to 6, the wood is not damaged and there is no impairment of the good mechanical properties, such as the cross-breaking 100 strength of building timber or mining timber.

A preferred embodiment of the apparatus 105 which can be employed for carrying out the process according to the invention is illustrated in the drawings, with the proviso that, as mentioned initially, the wood is treated by dipping using a continuous procedure.

Figure 1 shows a side view of the apparatus with partial sections;

Figure 2 shows a vertical section through the apparatus in the plane II—II shown in Figure 1;

Figure 3 shows a horizontal section in the plane III—III shown in Figures 1 and 2;

Figure 4 shows an enlarged vertical detail section according to region IV in Figure 1 or 110 according to the section plane identified as IV—IV in Figure 3; and

Figure 5 shows a section along one arm of the apparatus according to the section plane identified as V—V in Figures 1, 3 and 4.

As is illustrated by Figure 1, the apparatus 125 consists of a vertical U-shaped tube 1, comprising two arms 2 and 3, which preferably have a rectangular tube cross-section of, for example, 0.6×2.0 m internal diameter. The two tube arms 2 and 3 are connected in a liquid-tight manner in

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their lower region via a curved base 4, which is likewise tubular and of rectangular cross-section. In the upper region, the two tube arms 2 and 3 are connected to one another via a bridge 5.

5 The U-shaped tube 1 thus comprises the two tube arms 2 and 3 with the curved base 4 all of which are intended to receive the aqueous formulation 14. The liquid level of the aqueous formulation 14 is 16 and is defined by the height 10 h of the effective liquid level, which can be 3 to 25 m high, which corresponds to an excess pressure of 0.3 to 2.5 bars.

For through-transport or for circulation of the wood 8, which is to be treated, a conveyor device 15 is provided in the form of chains 6, arranged alongside one another, and carrier rails 7, which are of C-shaped cross-section, are fastened to the chains 6 and are made of sheet metal with uniform and close perforations of large aperture.

20 The chains 6 and the carrier rails 7 are driven by a drive mechanism 9 in the direction of the arrows. The wood 8, which is to be treated, is thus conveyed once or several times through the aqueous formulation 14, which, for example, can consist of the components (a), (b) and (c) described initially.

According to the invention, the upper ends of the two tube arms 2 and 3 are arranged so that they are inclined inwards, so that the chains 6 are 30 in contact with the inside curves of the tube arms 2 and 3. The U-shaped tube is arranged on foundations 10 in a collecting tank 11. The dimensions of the collecting tank 11 are such that, should any leaks occur, the tank is 35 sufficiently large to hold the entire amount of the aqueous formulation 14. The apparatus is fed, for example, by hand from a platform 15. The pieces of wood 8 which are to be treated, are pushed from the side into the carrier rails 7 in the region 40 of the bridge 5 and then pass in the direction of the arrow into the inlet 17 of the U-shaped tube, i.e. into arm 2 of the U-tube. They are then moved continually downwards until they meet a first deflection pulley 19. The wood 8 to be treated 45 passes ever more deeply into the aqueous formulation 14, i.e. is subjected to a static excess pressure which is proportional to the depth below the liquid level 16 of the aqueous formulation 14.

After the deflection in the direction of feed by 50 the deflecting pulley 19, the wood 8 to be treated passes into the curved base 4 of the U-shaped tube 1. After it has passed through this it is deflected by a second deflecting pulley 19 and conveyed upwards in arm 3 of the U-tube and 55 emerges at the outlet 18 in the region of the bridge 5. The treated wood can be taken out again here, or alternatively the treatment can be repeated by leaving the wood in the carrier rails 7.

The bottom 12 of the curved base 4 is 60 cambered on both sides to slope downwards, so that impurities can collect in the bottom and can be drawn off via a cock 13.

The cock 13 is, however, also provided so that the aqueous formulation 14 can be run off after 65 use, that is to say can then be replenished or

70 changed.

Figure 2 shows manual feeding with the wood 8 to be treated and manual withdrawal of the treated wood 8'. However, feeding and withdrawal can also advantageously be effected by mechanisation. It can already be seen in this figure that, for example, an assembly of carrier rails 7 is arranged on two circulating chains 6, which are arranged alongside one another; only a few of these carrier rails are indicated.

75 The conveyor device in the form of the chains 6 and the carrier rails 7 is described with the aid of Figures 3, 4 and 5.

80 The carrier rails 7, which have a C-shaped cross-section, have perforations 25, which are close together uniform and along the entire length of the rails. In practice, the rails are bent to C-rails from a metal sheet with close perforations of high-permeability or large aperture.

85 However, continuous free longitudinal slits are left in a region 26 to facilitate an even better overflow of the wood 8, to be treated, by the aqueous formulation 14.

90 The width of this region 26 is such that this is smaller than the minimal height 27 of a piece of wood 8 to be treated. This ensures that the pieces of wood 8 which are to be treated are absolutely reliably fed by the conveyor device through the aqueous formulation 14 without their being able to become detached.

95 The carrier rails 7 are fastened to the chains 6 via brackets 28 and one or more fastening members 29. The chains 6 run on runners 30, in order to protect the inside walls of the arms 2 and 3 of the U-tube against wear.

100 Laterally, the conveyor device 6 and 7 is fed through guide rails 31 of angular cross-section.

In the examples which follow, percentages are by weight.

105 **Example 1**
Saligna timber which has a length of 60 cm, a diameter of 15 cm and a moisture content of 20.4% is dipped for 2½ minutes 13.4 m beneath the surface of a hot aqueous solution which is at 60°C, contains 160 g of ammonium dihydrogen phosphate per litre and has a pH value of 4.0. After this time, the timber is removed from the solution and allowed to drip for 2 minutes. The liquor pick-up is 22.4%. The wood has a phosphorus content of 0.90% and according to CSIR Report No. 50090596 (86) of May 1979 is to be designated flameproof. To test the resistance of the flameproof finish to rinsing, the timber is placed in tapwater at 25°C for 24 hours.

110 115 After this time, the phosphorus content of the wood (evaluated by determining the phosphorus content of the rinsing bath by elementary analysis) is still 0.68%. Accordingly, the wood is to be designated as having a permanent flameproof finish.

120 **Example 2**
The procedure of Example 1 is repeated, except that saligna timber which has a moisture content

of 30.8% (instead of 20.4%) is treated and the timber is dipped for 3 minutes (instead of for 2½ minutes) at 20°C (instead of 60°C) 13.6 m (instead of 13.4 m) beneath the surface of the ammonium dihydrogen phosphate solution. The liquor pick-up is 19.7% and the phosphorus content of the finished wood is 0.79% after dipping and is still 0.64% after rinsing in tapwater. The wood is to be designated as having a permanent flameproof finish.

Example 3

The procedure of Example 1 is repeated, except that saligna timber which has a moisture content of 30.8% (instead of 20.4%) is treated and the timber is dipped for 6 minutes (instead of for 2½ minutes), at 60°C, 13.6 m (instead of 13.4 m) beneath the surface of the ammonium dihydrogen phosphate solution. The liquor pick-up is 23.8% and the phosphorus content of the finished wood is 0.95% after dipping and is still 0.74% after rinsing. The wood is to be designated as having a permanent flameproof finish.

Example 4

Saligna timber which has a length of 60 cm, a diameter of 15 cm and a moisture content of 20% is dipped for 10 minutes 10 m beneath the surface of an aqueous solution at 25°C, the solution containing, per litre, 160 g of ammonium dihydrogen phosphate and 12 g of digested maize starch and having a pH value of 4.1. The liquor pick-up is 19%. The timber is then removed from the solution and air-conditioned for 10 days. The wood has a phosphorus content of 0.82%. In the test in an inclined tunnel furnace according to CSIR Report No. 50090598 (86) of May 1979, which is carried out under conditions which approximate to those encountered in practice for mining timber, the saligna timber according to the invention, in contrast to untreated saligna timber, has very good flame-retardant properties. After conditioning, some of the treated saligna timber is subjected to a rinsing test under conditions which approximate to those encountered in practice in gold mines, by spraying with water from a garden hose under pressure at 12-hour intervals, the spraying procedure being repeated 10 times. After the rinsing test, the treated saligna timber still has very good flame-retardant properties in the CSIR test described above.

Similar results before and after the rinsing test are obtained when the saligna timber is treated under the same conditions but using an aqueous solution which contains, per litre, 160 g of ammonium sulfate and 12 g of digested maize starch and has a pH value of 4.8.

Example 5

The procedure of Example 4 is repeated, except that saligna timber with a moisture content of 25% and an aqueous solution which contains, per litre, 213 g of ammonium dihydrogen phosphate, 29 g of digested maize starch and 10 g of urea and has a pH value of 4.2 are employed. The

liquor pick-up is 15%. The treated wood has a phosphorus content of 0.86% and, in contrast to untreated wood, in the indicated CSIR tunnel test, likewise has very good flame-retardant properties after conditioning and still has good flame-retardant properties after the rinsing test indicated.

Claims

1. A process for flameproofing hardwood using formulations containing aqueous flameproofing agent, which comprises treating hardwood under an excess pressure of 0.3 to 2.5 bars with aqueous formulations which contain

- (a) at least one flameproofing agent,
- (b) optionally at least one fixing agent and
- (c) optionally at least one blowing agent.

2. A process according to claim 1, wherein the wood is dipped 3 to 25 m deep into the formulation.

3. A process according to either of claims 1 and 2, wherein the wood is treated under a static excess pressure of 0.8 to 1.6 bars.

4. A process according to any one of claims 1 to 3, wherein the formulation contains, as component (a), mono- or tetra-boric acid or the sodium salts thereof, an ammonium salt of ortho- or metaphosphoric acid, ammonium bromide, ammonium sulfate, ammonium bisulfate or ammonium sulfamate, calcium chloride, calcium sulfate, magnesium chloride, magnesium sulfate, tin chloride, tin sulfate, zinc chloride or zinc sulfate, sodium chromate or sodium dichromate or aluminium hydroxide.

5. A process according to claim 4, wherein the formulation contains, as component (a), calcium chloride, magnesium chloride, borax, ammonium sulfamate, ammonium sulfate, ammonium polyphosphate, ammonium dihydrogen phosphate or ammonium hydrogen phosphate.

6. A process according to claim 5, wherein the formulation contains, as component (a), ammonium hydrogen phosphate or ammonium dihydrogen phosphate.

7. A process according to any one of claims 1 to 6, wherein the formulation contains, as component (b), a thickener of natural or synthetic origin or a reaction product of

- (b₁) urea, cyanamide or dicyandiamide,
- (b₂) formaldehyde or a formaldehyde donor,
- (b₃) optionally an ammonium salt and
- (b₄) optionally an alkylene polyamine of at most 18 carbon atoms or an acid salt thereof,

the reaction product being optionally in the form of solution in water or in an alkanol having 1 to 4 carbon atoms.

8. A process according to claim 7, wherein the formulation contains, as component (b), a digested etherified, esterified or modified maize, potato, wheat or rice starch or degradation products thereof, a pectin or flour of vegetable origin, a size of animal origin, alginic acid or a salt or ester thereof, a cellulose ester or ether, or a salt

thereof, a polyacrylic acid or a polyvinyl or polyacrylic derivative.

9. A process according to claim 8, wherein the formulation contains, as component (b), a digested starch or the hydroxyethyl derivative thereof, a guar flour or carob bean flour, bone gelatin, a sodium alginate, a methyl- or carboxyethyl-cellulose, or the sodium salt thereof, polyacrylic acid, or a sodium polyacrylate or ammonium polyacrylate, or a polyvinyl alcohol.

10. A process according to claim 7, wherein the formulation contain, as component (b), a reaction product of
 (b₁) urea, cyanamide or dicyandiamide,
 (b₂) formaldehyde or paraformaldehyde,
 (b₃) optionally ammonium chloride, ammonium acetate, ammonium formate, ammonium nitrate, ammonium hydrogen phosphate or ammonium dihydrogen phosphate and
 (b₄) optionally ethylenediamine or a halide thereof, the reaction product being optionally in the form of an aqueous-methanolic, aqueous-ethanolic or aqueous-isopropanolic solution.

11. A process according to any one of claims 1 to 10, wherein the formulation contains, as component (c), a water-soluble nitrogen compound which under the action of heat splits off at least ammonia and carbon dioxide.

12. A process according to claim 11, wherein the formulation contains, as component (c), dicyandiamide, guanidine, guanylurea, melamine or urea or a salt thereof.

13. A process according to either of claims 11 and 12, wherein the formulation contains component (c) if component (b) consists of a thickener.

14. A process according to any one of claims 1 to 13, wherein the formulation contains 20 to 300 g/l of component (a), 0 to 60 g/l of component (b) and 0 to 150 g/l of component (c).

15. A process according to claim 14, wherein the formulation contains 30 to 300 g/l of component (a), 1.5 to 30 g/l of component (b) and 10 to 100 g/l of component (c).

16. A process according to claim 15, wherein the formulation contains components (a) and (b) in a weight ratio (a):(b) of 1:0.02 to 1:0.3.

17. A process according to claim 16, wherein the formulation contains components (b) and (c) in a weight ratio (b):(c) of 1:0.03 to 1:0.6.

18. A process according to any one of claims 1 to 17, wherein the formulation is in the form of an aqueous solution.

19. A process according to claim 18, wherein the pH value of the formulation in the form of an aqueous solution is 4 to 6.

20. A process according to any one of claims 1 to 19, wherein the wood is treated with the formulation at 10 to 90°C.

21. A process according to claim 20, wherein the wood is treated at room temperature.

22. A process according to any one of claims 1 to 21, wherein the wood is treated with the formulation for 1 to 30 minutes.

23. A process according to claim 22, wherein the wood is treated for 2 to 12 minutes.

24. A process according to any one of claims 1 to 23, wherein the hardwood employed is eucalyptus wood.

25. A process according to claim 24, wherein eucalyptus wood is employed in the form of hard gum or salligna timber.

26. A formulation for carrying out the process according to any one of claims 1 to 25, which contains components (a) and (b), components (a) and (c) or components (a), (b) and (c).

27. The hardwood provided with a flameproof finish by the process according to any one of claims 1 to 25.

28. The use of the hardwood according to claim 27 as pit timber in mining.

29. An apparatus for carrying out the process according to any one of claims 2 to 25, which comprises a substantially vertical conical U-shaped tube, which contains the aqueous formulation with a liquid level 3 to 25 m high, the tube having a conveying device of perforated metal sheets permeable to the formulation, for circulation of the wood to be treated, the said metal sheets taking up the wood at the inlet of the U-shaped tube and feeding it through the formulation to the outlet of the U-shaped tube.

30. A process according to claim 1, substantially as hereinbefore described, with reference to any one of the foregoing Examples.

31. Apparatus according to claim 29, substantially as hereinbefore described, with reference to and as illustrated in the accompanying drawings.